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TECHNICAL REPORT 3282

RADIATION-ENHANCED SURFACE
ACTIVITY OF GAMMA HMX

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FEBRUARY 1966

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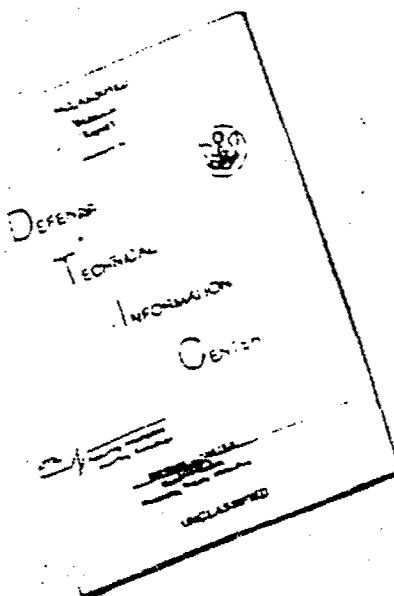
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by

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ABSTRACT

The surface activity of one-micron particle size γ -octahydro-1,3,5,7-tetranitro-s-tetrazine (γ -HMX) is enhanced by cobalt-60 gamma irradiation. Surface activity was measured by a radiometric determination of adsorption of carbon-14 labeled stearyl trimethyl ammonium bromide (STAB) from solution. At doses ranging from 5 to 60 Mrads, the enhanced surface activity is shown to be related to dose and the evolution of composite gaseous products derived from bulk as well as surface molecules. Although a one-Mrad irradiation of γ -HMX in vacuo produces no change in surface activity, such an irradiation of γ -HMX in contact with water vapor results in an enhancement of surface activity that is comparable to the effect of a 15-Mrad dose. Exposure of γ -HMX to NO_2 and NO increases surface activity by 28% and 42%, respectively; irradiation of these samples with one Mrad gives no additional enhancement.

The increased rate of thermal decomposition is not specific to radiation-enhanced surface activity promoted by water vapors but is found to be a function of gamma-ray interaction with bulk molecules as well. However, the increased rates of thermal decomposition of unirradiated samples of γ -HMX exposed to NO and NO_2 are attributed solely to thermally unstable reaction products of NO-HMX and NO_2 -HMX surface adducts.

INTRODUCTION

In the simplest case, a surface ion or molecule of a solid has at most five-fold coordination while its subjacent neighbor has a completed coordination number of six. The interatomic distances, either between ions or within a given molecule, are related to the prevailing fraction of the normal coordination number for a particular system. From six-fold coordination of ions within the crystal to single vapor molecules, the Na-Cl distance decreases from 2.81 to 2.51 Å. In agreement with this observation, the areas of surface layers are shown to be less than those of the internal layers. As a result, the binding forces as well as the distances in the surface layer are different from those in the interior of the crystal. In addition, changes in the internuclear distances affect the state of polarization of ion . Accordingly, the thermal vibrations of ions or molecules in

surface layers are less harmonic and hence the electron density distributions are less symmetrical than those located in bulk.

The description of the surface layer of a solid as containing ions or molecules in a lower than normal coordination and having internuclear distances different from those in the bulk of the solid does not in itself supply the key to a better understanding of surface chemistry. The relationship between reaction rates and the structure of a surface layer under stress would provide additional information. The bulk properties of macroscopic crystals composed of approximately 10^8 atoms in depth cannot be affected drastically by differences which exist between the structure of the interior and that of a surface layer. However, even for macrocrystals, rate phenomena that are initiated in the surface are likely to be influenced by such differences in spite of the infinitesimal ratios of surface to bulk volumes. The reactivity of solids which are surface initiated is highly sensitive to changes induced by the screening of the surface with adsorbed atoms or molecules.

In the screening process, an approach to the normal coordination number is achieved. The electron clouds of the adsorbed species supply the geometric balance necessary for greater symmetry of electron distributions within the surface layer. A nascent surface is under physical tension because of the tendency of the atoms or molecules to assume closer packing. Adsorbed species which can improve the screening of the solid decrease the state of tension by causing the surface layer to expand. In the dry state, the surface of nitrogen iodide is unsymmetrical and as such is unstable. As a result of this surface instability the solid particles are easily detonated and in some instances detonate spontaneously. However, when a water film is deposited on its surface nitrogen iodide becomes stabilized.

melting points and phase transitions of solids can be changed by molecules which are good screeners. Correlations have been made of solid-state reactions with van der Waals forces of various ambient atmospheres. The reaction $\text{MgO} + \text{F}_2\text{O}_3 \rightarrow \text{MgFe}_2\text{O}_4$ proceeds very slowly at a given temperature in a vacuum, whereas in the presence of gases the rate is greatly accelerated. The greater the van der Waals forces of the physically adsorbed gases (Ar, N_2 , etc., (i.e., the more the surface resembles the ideal crystal, the greater was the observed reactivity of the solids.

The screening of surfaces possessing highly polarizable and thermodynamically stable anions and highly polarizing cations induces changes in the mutual electronic interactions of the ions (continuous polarization). Thermodynamically, there is little difference between $\text{Hg}(\text{N}_3)_2$ and $\text{Ba}(\text{N}_3)_2$ because the energy is vested in the labile electronic structure, N_3^- . But the tendency for Hg^{++} to extract an electron from N_3^- is much greater than it is for Ba^{++} . The difference in behavior between the transition metal and alkali/alkaline earth metal azides is based on the ease of this continuous polarization. Crystals of $\text{Hg}(\text{N}_3)_2$ remain stable as long as the surface is screened with water. Removal of water creates a less symmetrical surface film in which the electronic interaction is increased to such an extent that the crystal detonates. Cupric acetylide (CuC_2) detonates on heating. But if the surface symmetry is increased by partial oxidation into CuO , the crystal decomposes on heating without detonating.

The examples cited above (Ref 2) show that the inherent differences which exist between the structure of the "perfect" crystal and that of its surface layer in which the initiating processes exist is indeed of chemical significance and that reaction rates in such cases can be affected by changes induced at the surfaces. It should be emphasized, however, that the study of the relationship of surface properties to bulk properties has been confined primarily to inorganic systems. Little or no work has been done in relating the two properties for organics or explosives (inorganic as well as organic). In fact, there is no definite proof that such a relationship even exists. Knowledge of the existence of such a relationship would help to indicate how the condition of the surface of an explosive affects the explosive process and would also supply practical information on altering the sensitivity of explosives.

It is conceivable that the physical and chemical properties of explosives can be altered in a desired direction by changes induced at the surfaces. By controlled exposure of the surface to adsorbate species it is possible to elucidate the mechanism of autocatalytic decomposition. As another example, by using soft electromagnetic radiation, it may be possible to induce the formation of a mono-layer polymeric film on the surface of an explosive. In the case of explosives normally sensitive to electrical and frictional energies, the threshold of initiation may be raised to a desired level by the deposition of a polymeric coating. The polymer (e.g., polystyrene) not only forms a protective coating by virtue of its inertness, but may also stabilize the explosive by the screening effect of the high electron density existing

between the carbon cores. In addition, such a protective coating may be effective in reducing the electrostatic interaction between particles. Such a reduction may be desirable in the formulation of some explosives compositions.

This report describes a preliminary phase study of the relationship of induced changes in surface activity to the thermal decomposition of γ -HMX. A radiometric solution adsorption method developed in this laboratory (Ref 1) was used to indicate the changes induced at the surface of γ -HMX by cobalt-60 gamma radiation.

EXPERIMENTAL

Preparation of Fine Particle HMX

Gamma-HMX was precipitated rapidly in water as a textured powder from a solution of 10 g HMX in 25 ml dimethyl sulfoxide (DMSO). The precipitate was immediately filtered and washed; it was then placed on absorbent paper to accelerate drying. The polymorph of HMX prepared in this manner was shown by infrared and x-ray analyses to be of the gamma form.

The average particle size of this material was found by electron microscopy to be about 0.65 micron. This value is in reasonable agreement with the particle diameter of 0.90 micron calculated from the observed BET surface area of 2.6 m²/g.

Surface Areas

Measurements were made by the BET method of low temperature (-196°) adsorption of N₂ and or Ar.

Gas Analyses

The identification of gaseous products of radiolysis was performed by mass spectrometry under a service contract with Gollob Analytical Services, Berkeley Heights, New Jersey.

Determination of Changes in Surface Activity

Changes in surface activity were determined (as a function of changes in saturated adsorptions of carbon-14 labeled stearyl trimethyl ammonium bromide (STAB) from solution) by the radiometric method previously reported (Ref 1).

Measurement of Trapped Gases

The release of occluded gases was done with DMSO as the solvent. Degassed DMSO and irradiated samples of HMX were mixed in a closed system affixed with a breakseal. After dissolution of the HMX, the solution was frozen at -78° and the gas pressure measured with a McCleod gauge. All volumes were adjusted to STP.

RESULTS AND DISCUSSION

Annealing Studies

To more effectively produce and determine changes at the surface, HMX of 0.65 micron particle size was used for this study. The reasonable agreement obtained between calculated and observed particle size indicates that this material is nonporous. Therefore, any adsorbate-STAB molecule interaction would be confined to the surface of the substrate, HMX.

Since the area covered by the STAB molecule at saturated adsorption is less than one half the total surface area of HMX (Ref 1), we have concluded that the adsorption of STAB occurs by means of an ionic interaction between STAB and a polar site. Therefore, any change in surface activity (active sites of a polar nature) produced by incident radiation could be measured by the corresponding change in the saturated-adsorption values of STAB. The normal coverage for STAB (approximately 30%) would make it possible to detect deviations from this value in either direction. Objections to the method may be based on the possibility of sintering of fine particles of γ -HMX in the solvent system of the adsorbate, STAB. The changes produced on the surface of γ -HMX could conceivably be annealed by contact with a liquid phase. The experiments summarized in Figure 1 (p 19) were conducted to determine the variable parameters involved and to establish conditions that would minimize the effects of these variables.

A number of separate samples of the STAB-solvent system in contact with 0.65 micron γ -HMX were assayed for STAB content at various time intervals. The series consisted of unirradiated and irradiated HMX, both sets being subdivided into two portions, one of which was degassed and the other of which was not. For both sets, STAB is shown to desorb exponentially from the HMX surface as a function of time of contact with the adsorbate solvent. Although physical adsorption is clearly demonstrated in both cases it is quite obvious that the surface activity of the irradiated HMX is significantly enhanced (to the extent of displacement of the two sets of curves by approximately 70%). Within the range of surface activity measured by this solution adsorption method, there is no observable difference between the annealing effect of the solvent on the irradiated samples and its effect on the control samples. Therefore, the annealing process must be independent of the radiation effect and dependent on some other factor.

Optical microscopic measurements showed that, as desorption takes place with time in both sets, the particles of γ -HMX sinter from the initial size of 0.65 micron to an equilibrated size of approximately 10 microns in the span of 15 to 24 hours (the asymptotic portion of the curves shown in Fig 1). Concurrent with this change, the crystalline form of the HMX converts from γ to β , as shown by infrared analyses. The desorption of STAB, and hence the annealing process, can be attributed in either set to a decrease in the specific surface activity proportional to a decrease in surface area. The increase in crystal size corresponds in each set to a decrease of 0.4 mg STAB desorbed per gram of HMX.

An apparent difference in the rate of crystal growth exists between the irradiated samples that were degassed and those that were not degassed, whereas the comparable unirradiated samples show no similar difference. The difference in rates of crystal growth could be attributed to the formation of some polar surface constituents that are loosely bound and others that are not removed by degassing at ambient temperature. The presence of the former has a retarding effect on the rate of crystal growth, but the removal of the latter results in a rate curve which is similar to that of the control.

Where the two curves are superposable during the first hour of sample equilibration, these complicating and concurrent processes become negligible. The selection of a fixed period of one hour for the equilibration of

all samples gave reproducible data and rendered the solution adsorption method a useful tool for comparative measurements of surface activity.

No significant post-irradiation annealing of the enhanced surface activity of HMX was observed within a 50-day period. This stability is apparently independent of integrated dose over the 4- to 40-Mrad range. A significant decrease of surface activity was observed only after 96 days post-irradiation for a sample exposed to a 16-Mrad dose. Since all measurements were made within a 5-day period, annealing of radiation-enhanced surface activity was not considered as a variable.

The chemical stability of irradiated γ -HMX is illustrated in Table 1 (p 14). Both the type and quantity of the products of the radiolysis are constant and independent of post-irradiation time. Apparently, there are no secondary gas phase or gas-solid phase reactions; and there is no diffusion of any interstitial gaseous products of radiolysis to the surface within a 36-day period. In fact, only residual quantities of occluded gases are present, as will be shown later. Irradiated γ -HMX is, therefore, shown to be stable generally in exposures to products of radiolysis as well as to the atmosphere over the period of time studied.

Dose-Surface Activity Interrelationships

The radiation-enhanced surface activity of γ -HMX was studied as a function of integrated dose to establish optimum conditions for a maximum ratio of surface-to-bulk molecular interaction with incident gamma radiation.

Figure 2 (p 20) shows the effect of various doses of gamma rays on adsorption isotherms of STAB on HMX. The curves are all of the same type; but with increasing dose, the amount of adsorption rises more steeply with increasing concentration, and the eventual saturated adsorption at the plateau is higher. This indicates that the number of ion-dipole interactions between STAB and HMX increases with dose. Presumably, radiolysis of surface molecules produces groups of a more strongly polar character than normally exist in HMX. The surface area of the unirradiated HMX ($2.6 \text{ m}^2/\text{g}$) decreased 22% to $2.1 \text{ m}^2/\text{g}$ after 64 Mrads irradiation. But the corresponding specific adsorptions (unit area basis) increased from 0.65 to 1.3 mg STAB m^2 , respectively, or by a factor of two.

The dose dependence of saturated adsorption corresponding to radiation-enhanced surface activity is shown in Figure 3 (p 21). There is an induction period for radiation-enhanced surface activity during the first 5 Mrads. Of particular interest is the fact that one Mrad is the maximum dose to which γ -HMX can be exposed without undergoing changes in surface activity as indicated by STAB adsorption. After an irradiation period of 5 Mrads, there is a linear relationship between dose and surface activity. The "y" intercept of this line is approximately 1.9 mg STAB/g HMX.

When the surface activity is plotted versus the composite gaseous products of radiolysis (Fig 4, p 22), the extrapolated linear portion of the curve following an induction period also intercepts the ordinate axis in the region of 1.9 mg STAB/g HMX. Apparently, integrated dose and evolved composite gaseous products are related to enhanced surface activity.

When the Compton interaction of gammas with matter is taken into consideration, the observed interrelation cannot be attributed to evolved gases derived solely from radiolyzed surface molecules. Because gas evolution and dose are related to surface activity in the same manner, the assumption is made that gaseous products of radiolysis, as derived from bulk as well as surface molecules, are being evolved from approximately one-micron γ -HMX. Urizar (Ref 3) has indicated the reverse to be the case, presumably for large-particle β -HMX. Certainly, particle size would affect the degree of gas occlusions.

To verify the above assumption, the dependence of radiation-induced gas evolution on particle size in terms of surface area, Σ , is presented in Table 2 (p 15). The difference in surface areas of the two samples studied is approximately one order of magnitude. No attempt is made to interpret the variations of the dose-dependent ratios of the constituent gases as a function of surface area. The combined disproportional volumes of evolved and trapped gases are shown to be independent of surface area but solely dependent upon integrated dose. The ratio of evolved gases as a function of decreasing surface area is much greater at the lower dose than at the higher dose, roughly 8 as against 3. The escape ratio (volume evolved/volume trapped) of the large-surface-area HMX is approximately the same for both doses. However, the escape ratio of the small-surface-area sample is very small and increases slightly from 0.1 to 0.5 with increased dose.

The conclusion drawn from these ratios is that the smaller the particle size, the greater the opportunity for gases to escape freely to the surface, and the larger is the escape ratio and the more independent of integrated dose. Based on $2.67 \times 10^3 \text{ \AA}^3$ for the molecular volume of HMX, as determined by Cady (Ref 4), and using a $0.65 \times 0.65 \times 1.64 \mu$ model corresponding to $2.6 \text{ m}^3/\text{g}$, the ratio of surface to bulk molecules was calculated to be 1/300. Apparently, for a depth of roughly 300 molecules the diffusion rate of the gases is rapid enough for their evolution to the surface to be virtually complete soon after formation.

From 5 to 60 Mrads, the radiation-enhanced surface activity of γ -HMX, as determined by the saturated adsorption of STAB, is clearly a linear function of the dose-dependent evolution of composite gaseous products derived proportionately from surface and bulk molecules. The lack of enhanced surface activity at 1 Mrad suggests that the effect occurring at larger doses may result from the presence of gaseous products of radiolysis adsorbed on the surface of the γ -HMX. Conceivably at one Mrad the relative pressures of the reactive gaseous products are too low for adsorption to take place (see Fig 5, p 23). Allen (Ref 5) has shown that a gas phase in contact with a solid substrate can draw excitation energy from a considerable volume of solid. On an organic solid like HMX, radicals or atoms formed from excitation and decomposition of adsorbed molecules would react with the surface of the solid, producing abnormally active sites. The total dose of one Mrad does not by itself induce any measurable increase in polar sites as determined by the radiometric method. Therefore, any change in surface activity observed in samples irradiated with the same dose but while in contact with gases must be attributed to the presence of the gases.

Irradiation of HMX Gas Mixtures

To test this hypothesis, γ -HMX was irradiated with 1 Mrad in the presence of the various gases listed in Table 3 (p 16). In the presence of water vapor, the radiation does in fact enhance the saturated adsorption by 13%. Exposure to NO_2 and NO increases the adsorption without radiation, by 28% and 42%, respectively; exposure to 1 Mrad gives no additional enhancement. These results would imply that NO_2 and NO undergo chemical reactions with surface molecules of γ -HMX prior to irradiation and that the surface adducts resulting therefrom are stable when subjected to the 1-Mrad dose.

To shed additional light on the significance of these observed changes in surface activity, mass spectrometric analyses were performed on the gaseous products of radiolysis of the solid gas phase mixtures. The gas analyses are recorded in Table 4 (p 17). Data on the NO₂/HMX mixture were not available because NO₂ cannot be analyzed easily with the mass spectrometer. The ratio of major products of radiolysis for H₂O/HMX is identical to the ratio for vacuo/HMX. The only significant difference between these two systems is in the quantities of composite gases produced by radiolysis. The increased gamma interaction with γ -HMX in the presence of water is consistent with the observed surface activities listed in Table 3. The number of gaseous constituents is the same for unirradiated NO/HMX as for irradiated NO/HMX with the exception of minor quantities of H₂. There is apparently a dark reaction between NO and HMX that is common to the radiation-induced reaction. The CO associated with this reaction and the high ratio of N₂O to N₂ are not observed for any of the other systems.

Although radiation produces, as a function of NO pressure, 3 to 7 times the quantities of gases derived from the dark reaction, the respective specific adsorptions are the same. The type of polar sites produced by the dark and radiation-induced reactions might be the same, but their number may differ. The 12% increased adsorption represents, roughly, 50% coverage of the γ -HMX surface area. Because of steric hindrance, this coverage may be considered maximum for STAB. Presumably, though additional polar sites may exist, they cannot accommodate any more STAB molecules because of the already saturated condition of the surface of the γ -HMX.

Thermal Decomposition Studies

In an attempt to relate changes in surface properties to bulk behavior, a study was made of the thermal decomposition rates of these samples of γ -HMX showing enhanced surface activities, as indicated in Table 3. The results of this study are shown in Table 5 (p 18). Because the acceleratory rate, k_a , of irradiated vacuo/HMX is 17% greater than that of unirradiated vacuo/HMX, no significance can be ascribed to the 17% increase in k_a of irradiated H₂O/HMX, NO/HMX, and NO₂/HMX. Of noteworthy interest are the percent inflection points of irradiated NO/HMX, vacuo/HMX, and NO₂/HMX, which are 11, 38, and 17, respectively, as compared to 47% for unirradiated vacuo/HMX. The order of sustained acceleratory period is

$\text{NO}_2/\text{HMX} > \text{NO}/\text{HMX} > \text{vacuo}/\text{HMX}$. Any interpretation of this order is undoubtedly complicated by the combined effects of radiation and enhanced surface activity. That the latter effect can play a role in the thermal decomposition rate is discussed in the next paragraph.

The NO/HMX and NO_2/HMX which were not irradiated and showed enhanced surface activity (42% and 28%, respectively) are representative of changes that have been induced solely and selectively at the surface. Therefore, comparison of their thermal decomposition rates with that of the control, unirradiated vacuo/HMX , is considered valid. The acceleratory rate of thermal decomposition of both these samples is 8% greater than that of the control and the acceleratory period is 4% shorter.

The adsorption studies have shown that one-third of the total surface area of HMX is covered by the STAB molecule. The unit cell of γ -HMX, according to Cady (Ref 4) and Pepinsky (Ref 6), has freely extended polar NO_2 groups at each end, and NO_2 groups which are somewhat shielded (via intermolecular hydrogen bonding) on four sides. This could account for the one-third coverage by STAB since the suggested mode of adsorption for quaternary salts is an ion-dipole interaction. Similarly, the NO and NO_2 vapor molecules could be interacting chemically with the one-third of the surface that is hydrophilic, producing thermally unstable molecular species of the type: R-NH_2 , RCHO , RCH_2OH , and RNHNO_2 . The presence of these species on the surface in such restricted concentrations conceivably could increase the acceleratory rate of thermal decomposition to the extent observed.

CONCLUSIONS

The radiation-enhanced surface activity of HMX as determined by saturated adsorption of STAB from solution is a function of the dose-dependent evolution of composite gaseous products derived from both surface and bulk molecules.

Gamma irradiation at low doses has been shown to interact nonspecifically with γ -HMX in the presence of paramagnetic gas molecules.

Increases in the rate of thermal decomposition of γ -HMX which has been exposed, without irradiation, to NO and NO₂ are attributed to thermally unstable reaction products of NO-HMX and NO₂-HMX surface adducts.

Although the radiometric method of STAB adsorption from solution has served effectively to indicate qualitatively the changes that take place at the surface of HMX, it has serious inherent limitations. The water-alcohol adsorbate system as a condensed phase in contact with the adsorbate produces a myriad of interactions competitive with the adsorbate-adsorbent adsorption potential. This report has demonstrated that these complex interactions have a strong annealing effect on active polar sites and that increases in the number of polar sites within the effectively large area covered by STAB are not detected.

RECOMMENDATIONS

The dark reaction existing between NO (and presumably also NO₂) and HMX may prove effective in inducing changes of a permanent nature (chemisorption), preferably at the surface. Another possible method of accomplishing this would be by the activation of gas molecules to their excited or dissociated states with electrodeless discharge in close proximity to the solid phase for efficient gas-solid interactions. The use of 2-6 ev energy electrons with half-thickness absorptions of one to two molecular diameters could also conceivably induce changes confined to surface molecules.

By means of a BET apparatus, surface properties can be more precisely measured and quantitatively compared on a unit area basis. The system of measuring is relatively simple, consisting of a gas phase in contact with the solid material. Heats of adsorption can be obtained from multi-temperature isotherms (isosteric heats of adsorption). From adsorptions at low relative pressures, energy site distributions can be calculated. With immersional heats in conjunction with preadsorbed quantities of water vapor, enthalpies, free energies, and entropies of adsorption can be determined (Ref 7). Such thermodynamic surface properties would be most sensitive to induced changes and amenable to quantitative measurements. In this manner surface activities can be more effectively compared to bulk properties of metastable materials.

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TABLE 1

Post-irradiation stability of gamma-HMX^a

Gaseous ^b Products	cc (Gas) STP $\times 10^3$ /g HMX with Post-Irradiation Time (Days)						
	Control ^c	3 days	4 days	6 days	10 days	24 days	36 days
H ₂	0.004	4.3	5.0	5.9	6.0	4.0	3.3
CO		25.7	28.6	30.0	30.0	32.9	27.1
N ₂	0.017	365.7	375.7	407.1	407.1	442.9	358.6
NO	0.023	91.4	88.6	111.4	111.4	121.4	111.4
N ₂ O		60.0	60.0	72.0	72.9	75.7	72.9
CO ₂	0.051	35.7	38.6	47.1	47.1	61.4	55.7
Mass 52 ^d		0.6	0.6	0.7	0.8	0.8	0.7
Total	0.096	583.4	597.0	675.3	675.4	739.1	629.7

^a 7 μ samples (average particle size $\sim 0.1 \mu$) from a common batch preparation, evacuated and irradiated at same time for 16 hours ~ 16 Mr.

^b As determined by mass spectrometric analysis.

^c Evacuated at same time and in same manner as irradiated samples; analysis performed at end of serial analyses.

^d An organic constituent not identified (possibly cyanogen, NC-CN).

TABLE 2

Radiation-induced gas evolution as a function of surface area of gamma-HMX

Dose, Mrad	Σ , m ² /g	cc (Gas) STP $\times 10^3$ /g HMX						Composite Volume ^a Evolved	Composite Volume ^b Trapped	Total Volume Produced	Percent Volume Trapped
		CO ₂	N ₂ O	CO	N ₂	NO	H ₂				
15.2	2.70	38	54	15	429	124	4	664	54	718	7.5
	0.22	2	2	4	63	3	5	79	690	769	90
60.8	2.70	440	313	82	2429	333	8	3605	230	3835	6.0
	0.22	102	56	83	1028	18	15	1303	2430	3733	65

^aDetermined mass spectrometrically after radiolysis.^bReleased by dissolution in dimethyl sulfoxide and measured manometrically.

TABLE 3

Dependence of surface activity of γ -HMX on
irradiation with various gases

	Unirradiated γ -HMX				Irradiated ^a γ -HMX					
	2.3	2.1	1.9	2.1	2.3	2.0	2.1			
m ² /g										
Gas	H ₂ O	NO	NO ₂	Vacuo	H ₂ O	NO	NO ₂			
					1	2	1	2	1	2
Saturated	1.14	1.55	1.21	1.15	1.23	1.30	1.35	1.42	1.55	1.14
Adsorption	1.12	1.60	1.20	1.13	1.32	1.29	1.37	1.47	1.45	1.22
mg STAB/g HMX	1.15	1.46			1.29		1.42	1.64		1.24
	1.14	1.33			1.32		1.49	1.66		
Average Adsorption unit Σ^b	0.50	0.71	0.64	0.54	0.56	0.57	0.71	0.76	0.71	0.57

^a Dose = 1 Mrad.

^b ± 0.04 mg STAB/unit area.

TABLE 4

Gaseous products from γ -HMX irradiated with H₂O and NO

Dose, Mrad	Exposed to	cc (Gas) STP - 10 ¹ /g HMX							Total Volume
		N ₂	CO	N ₂ O	CO ₂	NO	H ₂ O 30 mm	H ₂	CH ₃ O, R-NH ₂
None	H ₂ O								
	NO	9.8	9.8	4.3	1.3	280 mm			25.2
One	Vacuo	43.0		7.3	5.0	11.6		0.5	0.7
	NO	27.5	27.5	16.0	5.0	53 mm		0.5	76.5
		69.3	69.3	47.3	12.6	167 mm		0.8	109.3
	H ₂ O	125.7		20.6	14.3	33.1	30 mm	1.3	196.0
		59.4		9.8	6.7	15.7	20 mm	0.6	92.7

TABLE 5

Thermal decomposition rates^a of γ -HMX
irradiated with various gases

Gas	Dose, Mrad	k_1^b , min ⁻¹ $\times 10^3$	k_2^c , min ⁻¹ $\times 10^3$	Inflex ^d Point, %
Vacuo		12.3	8.6	46.9
	1.0	14.3	8.6	38.3
H ₂ O		12.5	8.1	47.0
	1.0	14.8	9.4	39.1
	1.0	14.7	9.2	38.3
NO		13.3	7.8	43.4
	1.0	13.8	9.0	40.7
	1.0	14.1	9.8	42.0
NO ₂		13.2	8.5	43.8
	1.0	14.0	9.7	48.6
	1.0	13.8	10.1	47.7

^a Values significant to ± 0.2 .

^b Acceleratory rate of chain reaction.

^c Decay rate of first order residual HMX decomposition reaction.

^d Of acceleratory and decay rates.

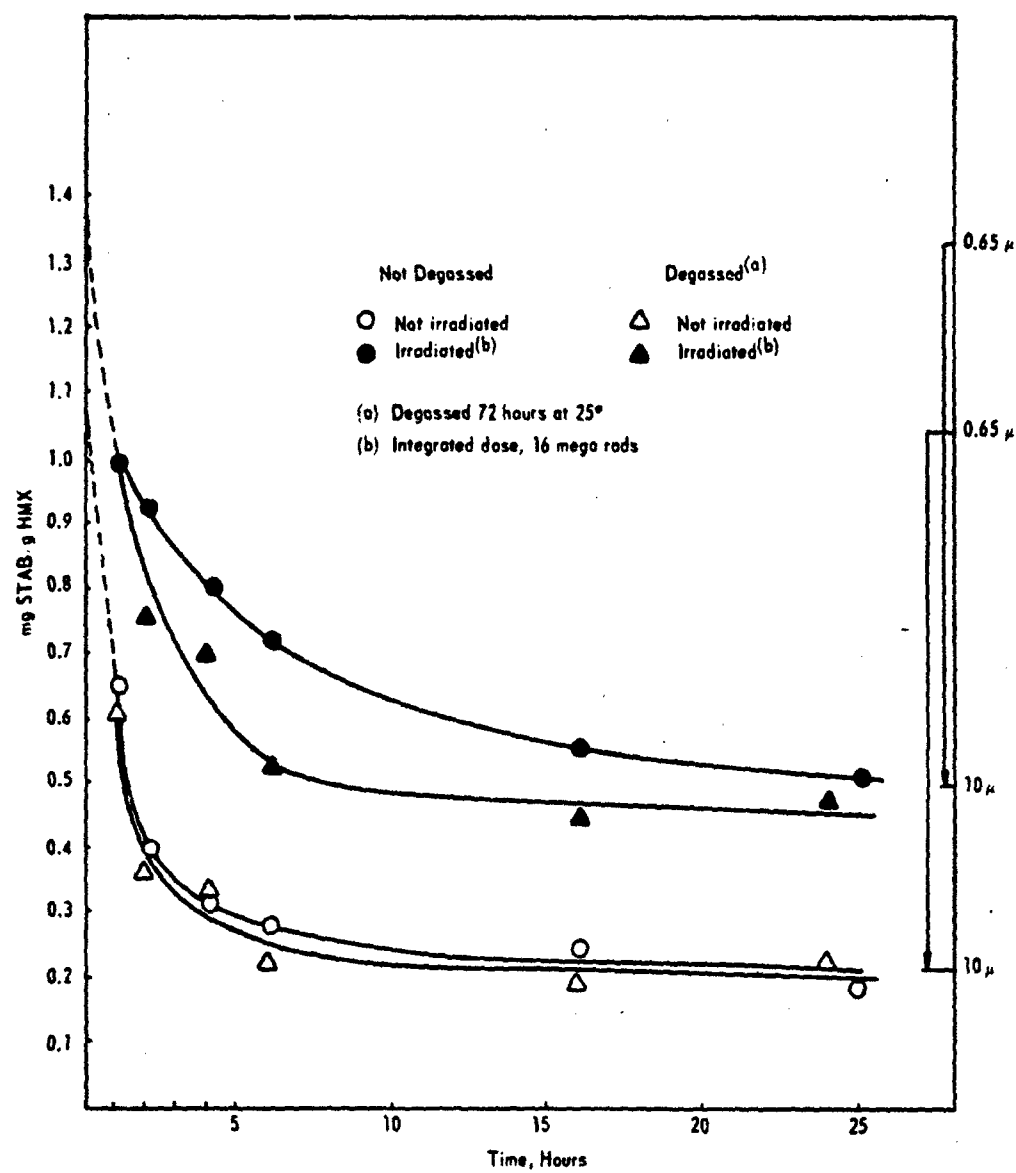


Fig 1 Effect of adsorbate solvent system on stability of particle size of irradiated and unirradiated 0.65 μ gamma HMX

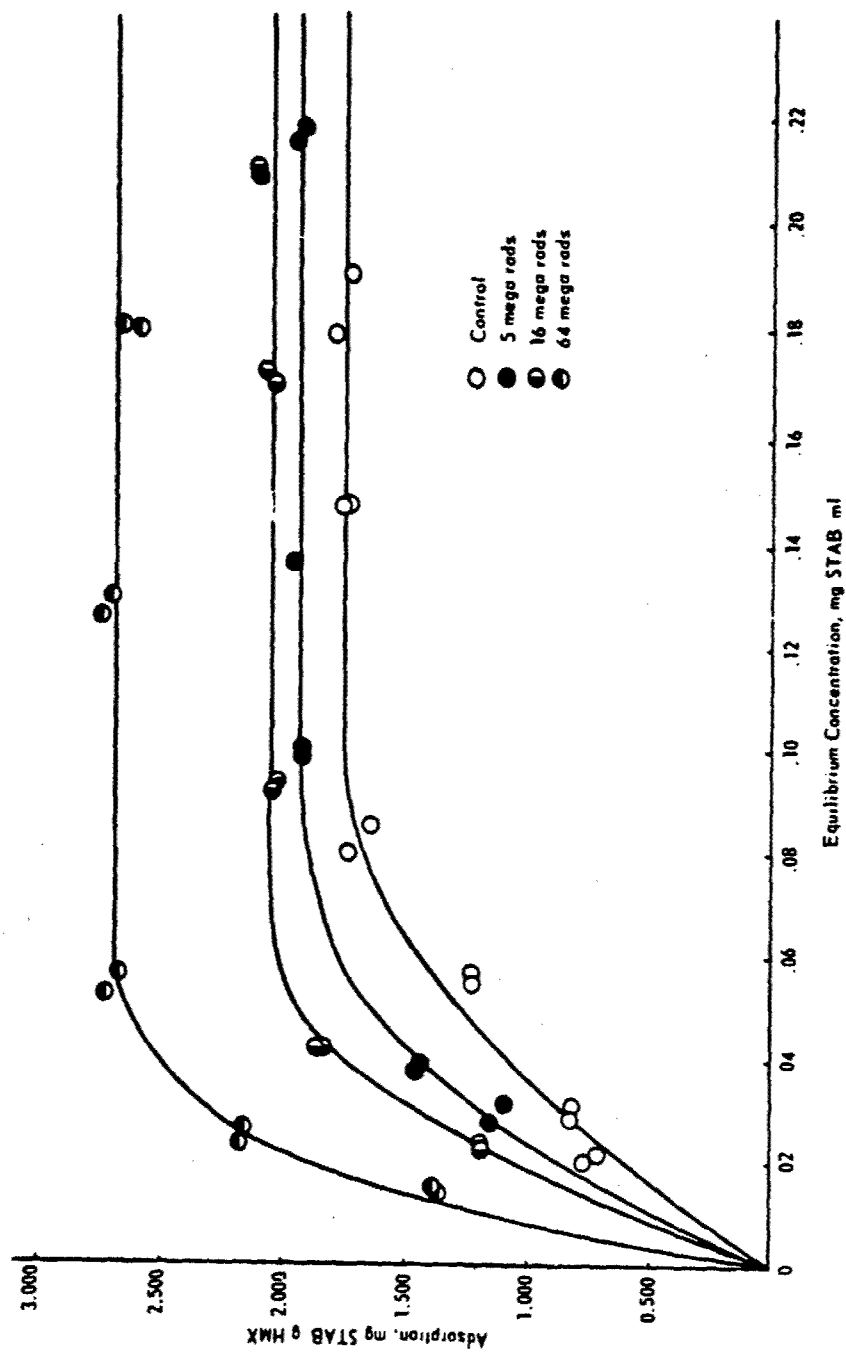


Fig 2 Adsorption isotherms of cobalt-60 gamma-irradiated HMX

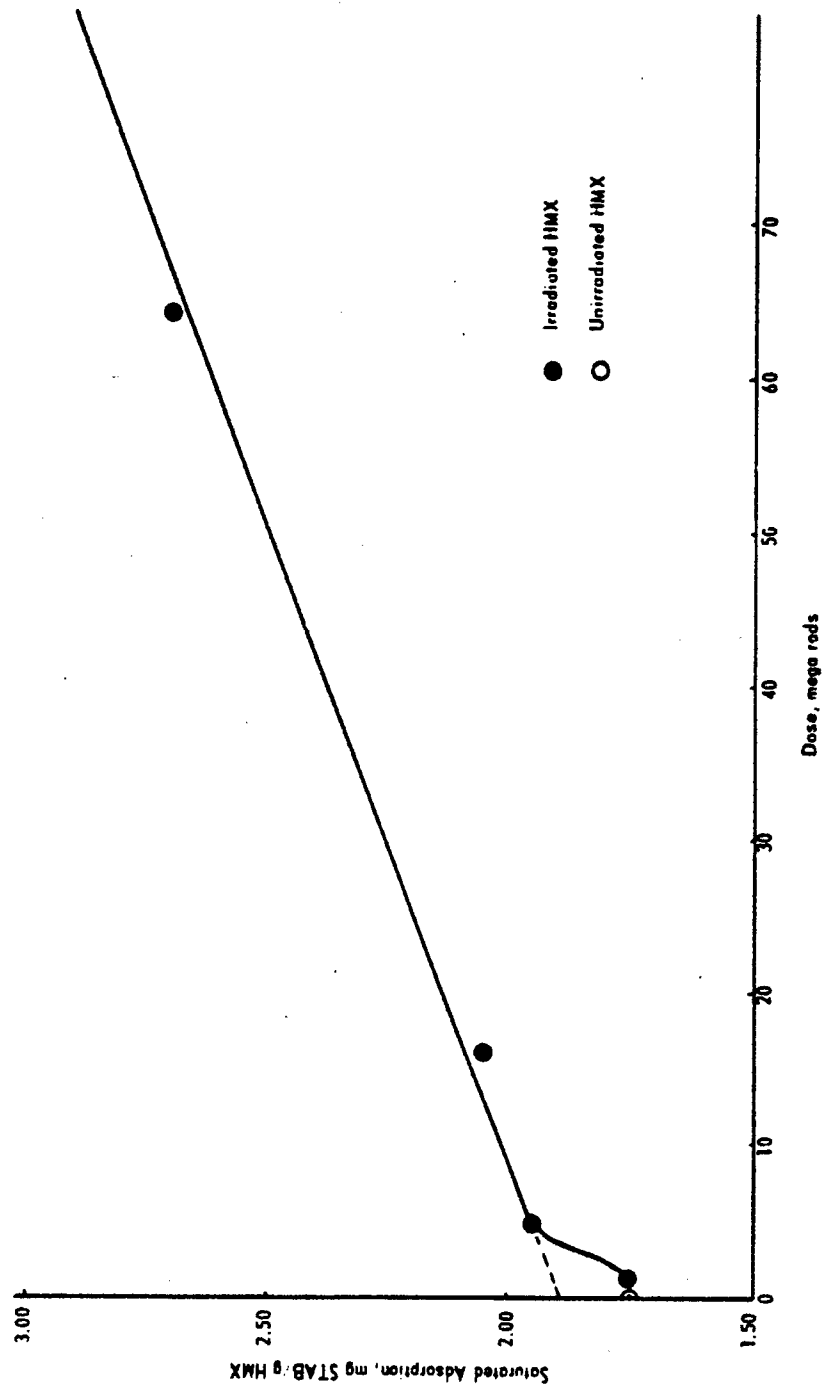


Fig 3 Dependence of surface activity of γ -HMX on integrated dose of gamma radiation

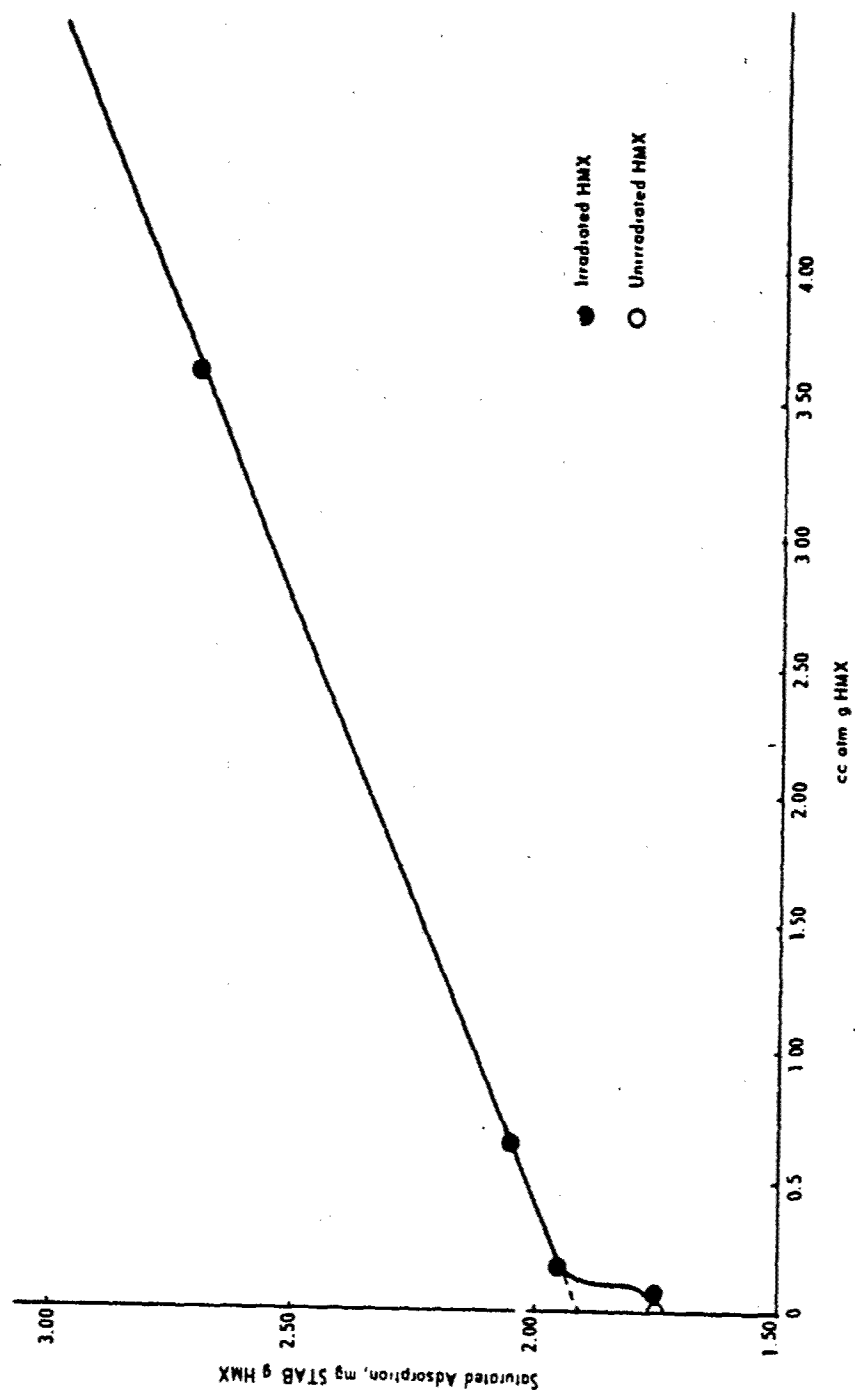


Fig 4 Dependence of surface activity of γ -HMX on composite gaseous products of gamma radiolysis

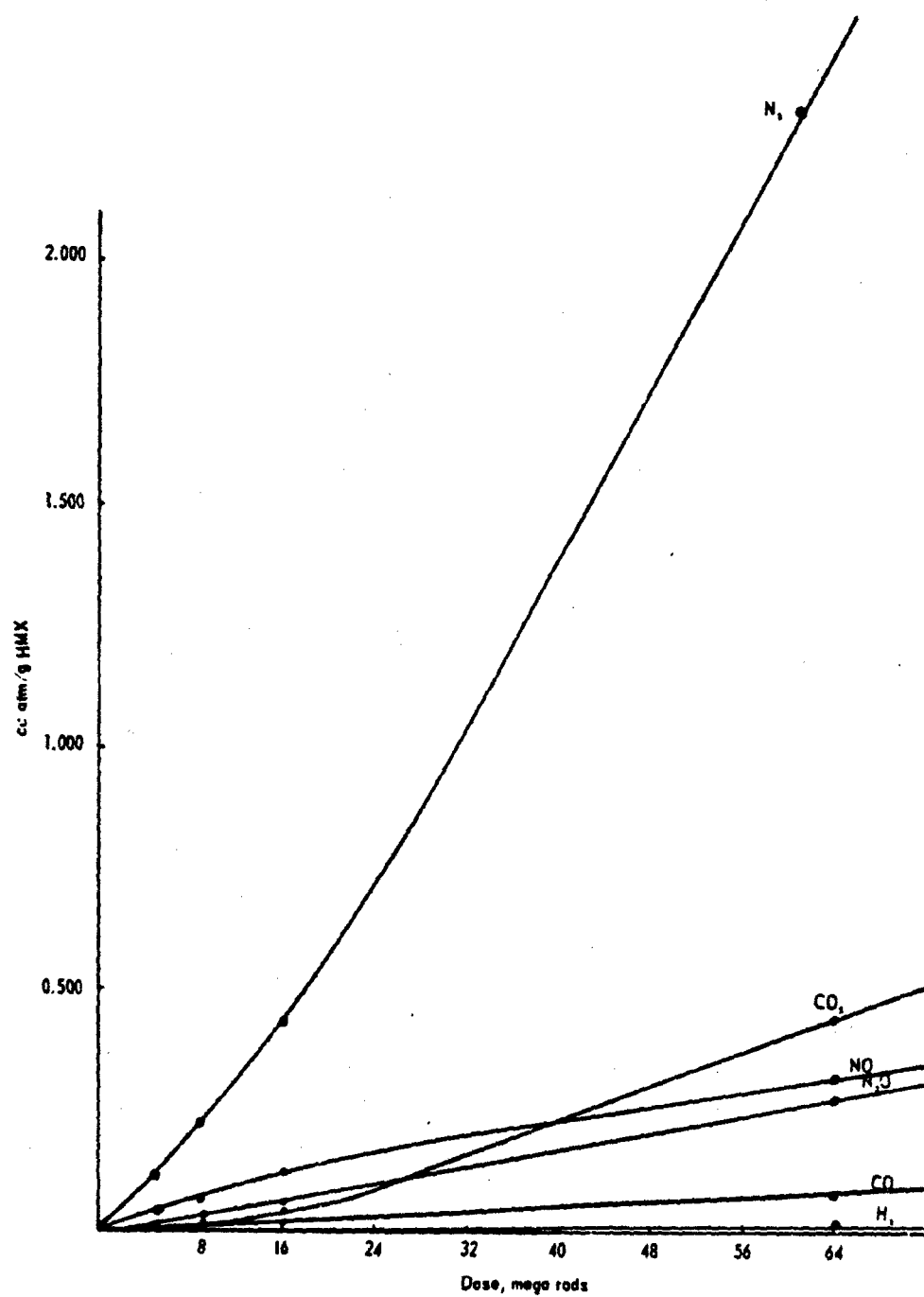


Fig 5 Gaseous products of Co⁶⁰ gamma radiolysis of γ -HMX

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<p>The surface activity of one-micron particle size γ-octahydro-1,3,5,7-tetranitro-s-tetrazine (γ-HMX) is enhanced by cobalt-60 gamma irradiation. Surface activity was measured by a radiometric determination of adsorption of carbon-14 labeled stearyl trimethyl ammonium bromide (STAB) from solution. At doses ranging from 5 to 60 Mrads, the enhanced surface activity is shown to be related to dose and the evolution of composite gaseous products derived from bulk as well as surface molecules. Although a one-Mrad irradiation of γ-HMX in vacuo produces no change in surface activity, such as irradiation of γ-HMX in contact with water vapor results in an enhancement of surface activity that is comparable to the effect of 15-Mrad dose. Exposure of γ-HMX to NO, and NO increases surface activity by 28% and 42%, respectively; irradiation of these samples with one Mrad gives no additional enhancement.</p> <p>The increased rate of thermal decomposition is not specific to radiation-enhanced surface activity promoted by water vapors but is found to be a function of gamma-ray interaction with bulk molecules as well. However, the increased rates of thermal decomposition of unirradiated samples of γ-HMX exposed to NO and NO₂ are attributed solely to thermally unstable reaction products of NO-HMX and NO₂-HMX surface adducts.</p>		

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Gamma HMX						
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Cobalt-60 gamma irradiation						
Radiometric determination						
Interatomic distance						
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